

Supporting Information for:

Assembly, Characterization, and Electrochemical Properties of Immobilized Metal Bipyridyl Complexes on Silicon(111) Surfaces

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Experimental Details

All chemicals were used as received, unless otherwise specified. Water with a resistivity $\geq 18.0 \text{ M}\Omega\text{-cm}$ was obtained from a Barnstead E-pure system. Acetonitrile and dichloromethane solvents were of commercial grade and were dried over activated alumina prior to use. Methanol, trichloroethylene, tetra-*n*-butylammonium hexafluorophosphate ((*n*-Bu)₄NPF₆; electrochemical grade), and *p*-toluenesulfonic acid were obtained from Sigma-Aldrich and used as received.

[Cp*RhCl₂]₂,¹ [Cp*IrCl₂]₂,¹ Cp*Rh(bpy)Cl₂,² Cp*Ir(bpy)Cl₂,³ Ru(acac)₂(coe)₂,⁴ and [Ru(acac)₂(bpy)]PF₆⁴ were synthesized following published methods. 4-vinyl-2,2'-bipyridyl (vbpy) was prepared using literature procedures, but was not purified using column chromatography. Instead, vbpy (*ca.* 90%) was used as prepared.⁵

Single-side polished, degenerately B-doped, p-type Si(111) wafers that were $525 \pm 25 \text{ }\mu\text{m}$ thick and had a resistivity of 0.001-0.005 $\Omega\text{-cm}$ (Silicon Valley Microelectronics, Inc.), and double-side polished monocrystalline, As-doped, n-type Si(111) wafers that were $350 \pm 25 \text{ }\mu\text{m}$ thick, with a resistivity of 4–8 $\text{k}\Omega\text{-cm}$ (Topsil, Santa Clara, CA), were functionalized using techniques described previously.^{6,7,8,9,10} Copper foil (99%) was obtained from McMaster-Carr.

Preparation of functionalized silicon(111) surfaces

1. Preparation of Cl-terminated Si(111) Wafers. Si(111) wafer pieces of $\sim 1 \text{ cm}^2$ were immersed in boiling piranha solution (1:2 by volume of 10.1 M hydrogen peroxide (aq) and 18 M sulfuric acid) for 10 min, allowed to cool under ambient conditions, and rinsed with H₂O. The wafers were etched for 18 s in buffered HF (NH₄F/HF, Transene) and were then immediately transferred to a solution of 40% NH₄F(aq) (Transene) which had been degassed with Ar(g) for at least 30 min prior to use. After 15 min, the resulting H–Si(111) samples were rinsed with water and dried under a stream of N₂(g). The samples were then transferred to a N₂(g)-purged flush box, and immersed in a saturated solution of PCl₅ (Alfa Aesar, 98%) in chlorobenzene (Sigma-Aldrich, 99.8%) to which a few grains of benzoyl peroxide (Aldrich reagent grade, 97%, Sigma-Aldrich) had been added as a radical initiator. The solution and samples were heated to 90–100 °C for 45–60 min, and then the resulting Cl–Si(111) samples were removed from the solution, allowed to cool, and rinsed with tetrahydrofuran (THF, Sigma-Aldrich, $\geq 99.9\%$, inhibitor free).

2. Preparation of Methyl-Terminated Si(111) Surfaces. CH₃–Si(111) surfaces were produced by immersing Cl–Si(111) surfaces in 1.0 M CH₃MgCl (diluted with THF from 3.0 M CH₃MgCl, Sigma-Aldrich) at 65 °C for 2–3 h. The samples were rinsed with THF, then rinsed with methanol (Sigma-Aldrich, 99.8%) to remove and quench any unreacted Grignard reagent, and the resulting CH₃–Si(111) samples were then removed from the flush box.

3. Preparation of Mixed Methyl/Vinylferrocenyl-Terminated Si(111) Surfaces. Cl–Si surfaces were placed in 1.0 M CH₃MgCl for 10 min at room temperature, resulting in partial methyl termination of the surface. The wafers were then placed in a quartz cell containing a solution of $\sim 10 \text{ mg}$ vinylferrocene (vFc, Alfa Aesar) in $\sim 3 \text{ mL}$ dichloromethane (CH₂Cl₂, Alfa Aesar, 99.8%) to which a few grains of benzoyl peroxide had been added as a radical initiator. The cell was then exposed to UV light (254 nm, 18.4 watts) for 1 h. The samples were then

removed from the cell, rinsed sequentially with CH₂Cl₂, THF, and methanol, and then removed from the flush box.

4. Preparation of Mixed Methyl/Bipyridyl-Terminated Si(111) Surfaces. To prepare methyl-terminated surfaces, Cl-Si(111) surfaces were placed in 1.0 M CH₃MgCl for 5 min at room temperature. The wafers were then placed in a quartz cell that contained a solution of ~10 mg 4'-vinyl-2,2'-bipyridyl (vbpy) in ~3 mL dichloromethane (CH₂Cl₂, Alfa Aesar, 99.8%) to which a few grains of benzoyl peroxide had been added as a radical initiator. The cell was then exposed to UV light (254 nm, 18.4 watts) for 1–2 h. The samples were removed from the cell, rinsed sequentially with CH₂Cl₂, THF, and CH₃OH, and then removed from the flush box. Prior to characterization, all of the functionalized Si(111) samples were sonicated for 10 min sequentially in THF, methanol, and water.

5. Modification of the Mixed Methyl/Bipyridyl-Terminated Si(111) Surfaces with [Ru(acac)₂] Ru(acac)₂(bpy) (acac is acetylacetonate), which has an electrochemically reversible Ru(III)/Ru(II) couple, formed the basis for assembly of Ru complexes on the mixed methyl/bipyridyl-functionalized Si(111) surfaces. To prepare a Ru-modified surface, a mixed methyl/bipyridyl-functionalized Si(111) sample was immersed in a ~6 mM solution of Ru(acac)₂(coe)₂ (coe is *cis*-cyclooctene) in tetrahydrofuran (THF) under Ar(g) and heated to 100 °C for 12 h in a sealed pressure vessel. After cooling, the pressure vessel was opened to air, presumably resulting in oxidation of Ru(II) to Ru(III), and the samples were sonicated for 10 min each sequentially in CH₂Cl₂, CH₃OH, and H₂O.

6. Evaluation of the Stability of the Immobilized Rhodium Complexes. The stability of the Rh-modified mixed methyl/bipyridyl-functionalized Si(111) surface was evaluated under conditions where the [Cp*Rh] complex has previously been reported to act as a proton-reduction electrocatalyst.¹¹ Rh-modified samples were analyzed by XPS and then soaked for 1 h in 0.1 M (n-Bu)₄NPF₆ or in 0.1 M (n-Bu)₄NPF₆ in CH₃CN that contained 3 mM *p*-toluenesulfonic acid. The samples were then removed from the solutions, sonicated in CH₃CN for 10 min, and reanalyzed by XPS.

Instrumentation

1. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopic (XPS) data were collected using a Kratos AXIS Ultra system. The pressure in the sample chamber was kept at < 5 × 10⁻⁹ torr, and ejected electrons were collected at an angle of 90° from the surface normal. Survey scans were performed to identify the elements on the surface of the Si. Additionally, high-resolution spectra were collected for the Si 2p, C 1s, Fe 2p, Cl 2s, N 1s, Rh 3d, Ir 4f, and Ru 3p regions. The XPS data were analyzed using the program Computer Aided Surface Analysis for X-ray Photoelectron Spectroscopy, or CasaXPS. All XPS signals are reported as binding energies and are reported in eV. Ordinate axes are typically plotted as counts per second (CPS) and are in arbitrary units.

Surface Coverage Calculations. The CH₃-Si(111) surface was used as a reference to obtain an XPS C 1s:Si 2p signal-area ratio, Θ_{Me}, corresponding to a complete monolayer wherein every Si atop site was functionalized by a CH₃ group. Accordingly, on CH₃-Si(111) surfaces, the area of the C 1s peak at 284 eV, ascribable to carbon directly attached to silicon, was normalized by the

area of the Si 2p peak, and used as Θ_{Me} . 1.0 monolayer of coverage was therefore defined as having 100% of the Si(111) atop sites (7.8×10^{14} atoms cm^{-2}) functionalized by the element in question. To calculate the fraction of a monolayer of Si–C groups that were present on the mixed monolayer surfaces, the ratio of the area of the lowest-energy C 1s peak (at 284 eV) to the Si 2p peak area was divided by the value of Θ_{Me} . For example, the coverage of Rh on Si(111) surfaces, θ_{Rh} , was calculated by dividing the area of the Rh 3d peaks at 310 and 315 eV, which correspond to Rh in the +3 oxidation state, by the area of the Si 2p signal on such surfaces, and correcting for the relative sensitivity factor (RSF) of Rh 3d for our instrument. The ratio of θ_{Rh} to θ_{Me} gave the ratio of the number of Rh(III) atoms on the surface to Si(111) atop sites, i.e., the fraction of the surface that was functionalized by the Rh(III) complex.

The total amount of C on a given surface was estimated using the entire C 1s peak (i.e., adding the areas of all the C 1s components) normalized by the Si 2p signal. The surface coverage of chlorine, θ_{Cl} , was calculated similarly, using the area of the Cl 2s peak at 270 eV, correcting for the RSF for Cl, and normalizing by the area of the Si 2p signal on that surface. The ratio of θ_{Cl} to θ_{Me} gave the surface coverage of chlorine as a fraction of Si atop sites. Similar calculations were performed using the Fe 2p peaks at 708 and 721 eV to calculate the surface coverage of iron, the N 1s peak at 400 eV to calculate nitrogen coverage, the Ir 4f peak at 64–65 eV to calculate iridium coverage, and the Ru 3p peaks at 463 and 485 eV to calculate ruthenium coverage. The silicon oxide coverage was calculated by normalizing the area of the broad Si 2p peak at 101–105 eV corresponding to oxidized silicon⁶ by the area of the bulk Si 2p signal at 99–100 eV, correcting for the RSF for Si 2p for our instrument and then dividing by θ_{Me} .

2. Surface Recombination Velocity. Surface recombination velocity (S) measurements were made using a contactless microwave conductivity apparatus that has been described previously.^{7,8} A 20-ns pulsed-diode laser with a wavelength of 905 nm (OSRAM laser diode with an ETX-10A-93 driver) was used to generate electron-hole pairs in high-purity, nearly intrinsically doped Si(111) wafers. The lifetime of the photogenerated charge carriers was monitored using a PIN diode that detected the microwave radiation reflected from the sample. Functionalized surfaces that had been prepared using nearly intrinsic As-doped n-type Si(111) wafers were tested immediately after preparation, and for several days afterward. Between measurements, the samples were stored in the dark, in air.

Charge-carrier lifetimes were measured by fitting the excess charge-carrier density, A , to a single-exponential decay:

$$A = y_0 + ae^{-t/\tau} \quad (1)$$

The extracted lifetime, τ , was converted to a surface recombination velocity, S , using:

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{2S}{d} \quad (2)$$

where τ and τ_B are the measured and bulk lifetimes, respectively, and d is the wafer thickness. For high-purity Si, the bulk-carrier lifetime is much larger than the measured τ ($\tau_B^{-1} \ll \tau^{-1}$), which allowed the simplification:

$$S = \frac{d}{2\tau} \quad (3)$$

3. Electrochemistry. Electrochemistry was performed in a nitrogen-filled glove box using alumina-dried acetonitrile as the solvent and 0.10 M tetra n-butylammonium hexafluorophosphate ((n-Bu₄)NPF₆, Fluka electrochemical grade) as the supporting electrolyte. Measurements were made using a three-electrode configuration and a Princeton Applied Research Parstat 4000 potentiostat controlled by Princeton Applied Research VersaStudio v.2.2 (2012) software. The counter electrode was basal plane graphite (BPG) and the reference electrode was Ag/Ag⁺ (silver wire immersed in electrolyte, separated from the solution by a porous Vycor tip (Bioanalytical Systems, Inc.)). Ferrocene (99%, from Strem Chemicals) was added to the electrolyte solution at the conclusion of each experiment ([Fc] ~ 1 mM); the midpoint potential of the ferrocene/ferrocenium couple (denoted as Fc⁺⁰) served as an external standard for comparison of the recorded potentials. Voltammetry for the functionalized surfaces was performed by first scanning cathodically to sufficiently reducing potentials to observe the redox event of the immobilized metal complexes. Generally, the sweep width was from 0 to -1.5 V vs. Fc⁺⁰ at a scan rate of 100 mV s⁻¹.

Ohmic contact to the B-doped Si wafers was made by scratching the back of the functionalized wafer with a Ga-In eutectic and then placing the wafer on Cu foil supported by a stainless steel base. The wafers were then secured in a custom-made Teflon cell with an O-ring seal used to define the electrode area (0.28 cm²). This cell has been described previously.¹²

For obtaining surface coverages of the electroactive metals, a linear fit was used to subtract background current from the cyclic voltammograms. The anodic and cathodic waves were then integrated independently to estimate surface coverage. The area under the background-subtracted current-versus-time plot gave the total charge transferred to the immobilized metal complexes, which was then divided by the surface area to yield the number of electroactive groups per cm². The total number of electrochemically active groups per cm² divided by the surface density of silicon atop atoms on a (111) surface, 7.8 x 10¹⁴ atoms per cm², yielded the fraction of the Si atop sites covered by electroactive groups, or number of monolayers as previously defined.

Following electrochemistry, the surfaces were sonicated sequentially in CH₃CN, CH₃OH, and H₂O to remove any associated electrolyte. XP spectra were then collected to determine the species that remained on the surface.

4. X-ray Absorption Spectroscopy (XAS) Data Collection

Ir L_{III} XAS measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on Beamline 7-3 at an electron energy of 3.0 GeV and an average current of 500 mA. The intensity of the incident X-ray beam was monitored using a N₂-filled ion chamber (I₀) in front of the sample. A Si(220) double-crystal monochromator was used to detune to 50% of the maximum flux to attenuate higher harmonics. The data was collected as fluorescence excitation spectra with a Ge 30-element detector (Canberra). The monochromator energy was calibrated using Ir foil (a rising edge energy of 11215.00 eV).

The powder sample was diluted with boron nitride (1% w/w). The mixture was packed into 0.5 mm thick aluminum sample holders and sealed with Mylar tape. To ensure that no X-ray

induced radiation damage occurred, the L_{III} edge position was closely monitored for any reduction.

Data reduction of the XANES spectra was performed using SamView (SixPACK software, Dr. Samuel M. Webb, SSRL). The pre-edge and post-edge backgrounds were subtracted from the XAS spectra using Athena (IFEFFIT software), and the resulting spectra were normalized with respect to the edge height.

Additional XPS and Electrochemistry Data

Figure S1. High-resolution XP spectra for the Si 2p and Cl 2s region of the mixed methyl/bipyridyl Si(111) surface, as described in the main text. CPS is defined as counts per second, and are arbitrary units.

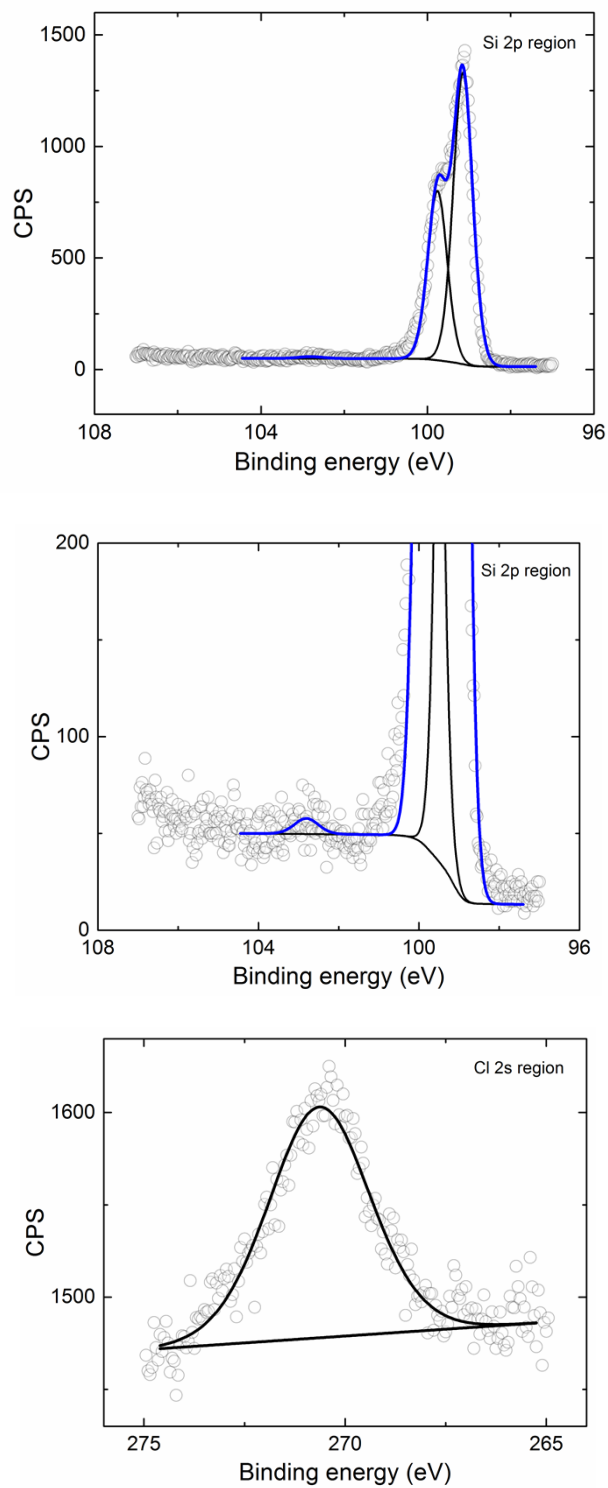


Figure S2. High-resolution XP spectra for the Rh 3d and Cl 2s regions of CH₃-terminated Si(111) exposed to [Cp*RhCl₂]₂ as described in the main text. Data are shown as gray circles.

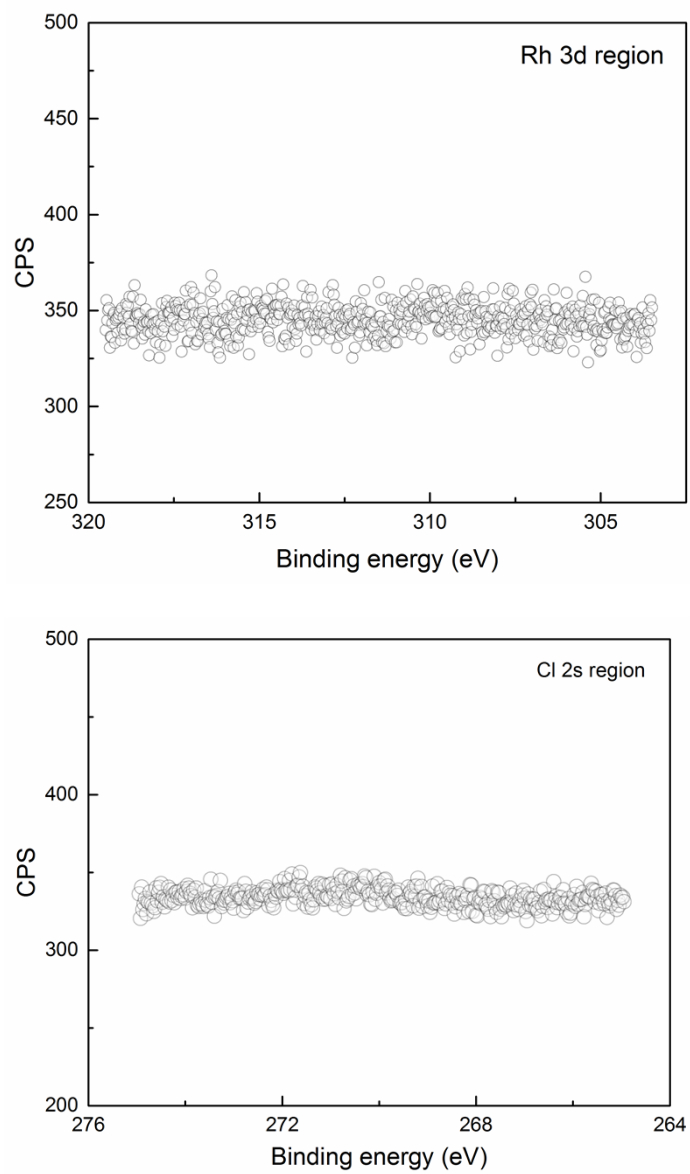


Figure S3. High-resolution XP spectra in the Rh 3d region for [Cp*RhCl₂]₂ drop-cast onto Cu foil. Data are plotted as gray circles, and the individual fits are the black lines. The complete fit made up of the individual components is the red line. Fit was accomplished with two sets of 3d doublets; each 3d_{3/2} peak area was constrained to 0.66 of the corresponding 3d_{5/2} peak.

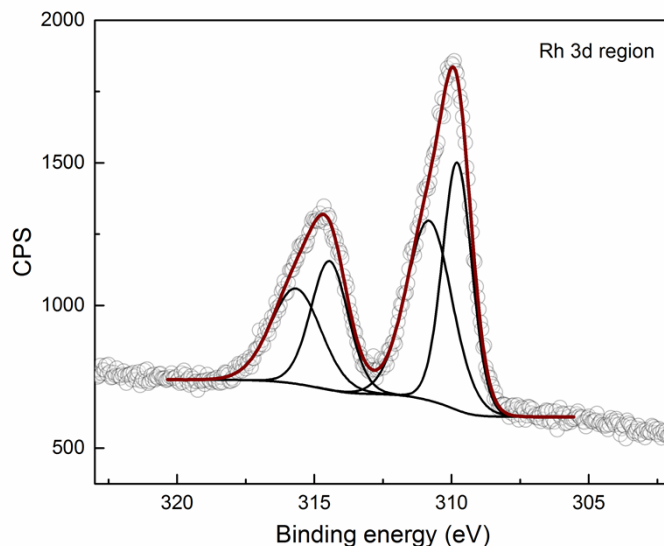


Figure S4. High-resolution XP spectrum in the Rh 3d region for the mixed methyl/bipyridyl surface on Si(111) exposed to a 20-mM solution of [Cp*Rh(bpy)Cl]Cl, as described in the main text. Data are plotted as gray circles, and the individual fits and Shirley background are the black lines. The complete fit made up of the individual components is a black line. The 3d_{3/2} peak area was constrained to 0.66 of the corresponding 3d_{5/2} peak.

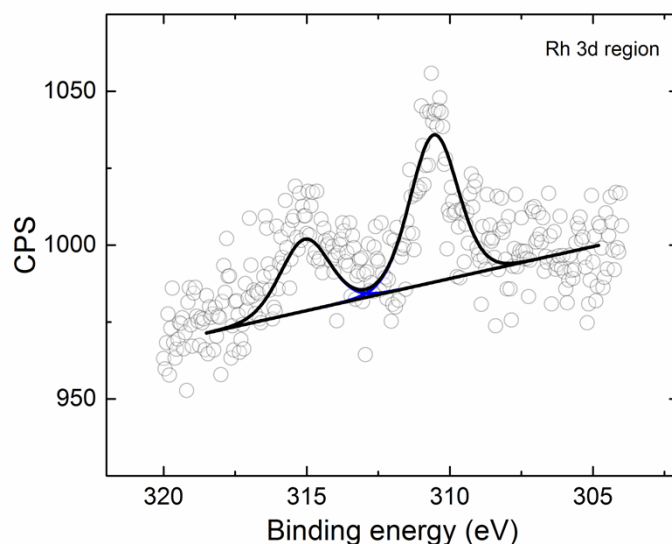


Figure S5. XP spectrum for a mixed methyl/bipyridyl surface exposed to $[\text{Cp}^*\text{IrCl}_2]_2$ for 1 h.

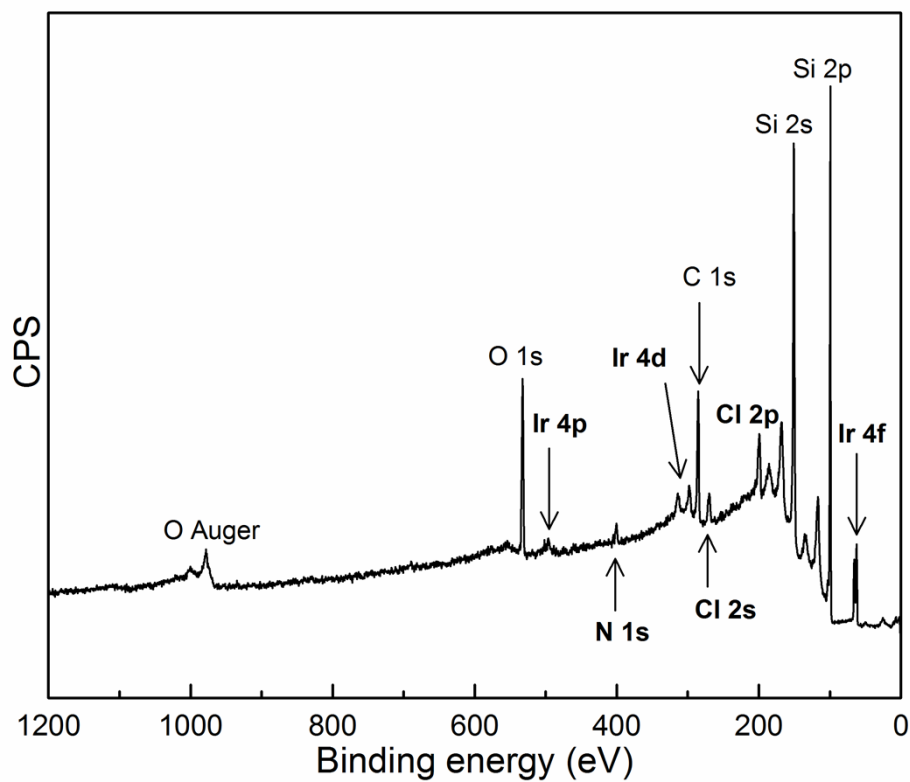
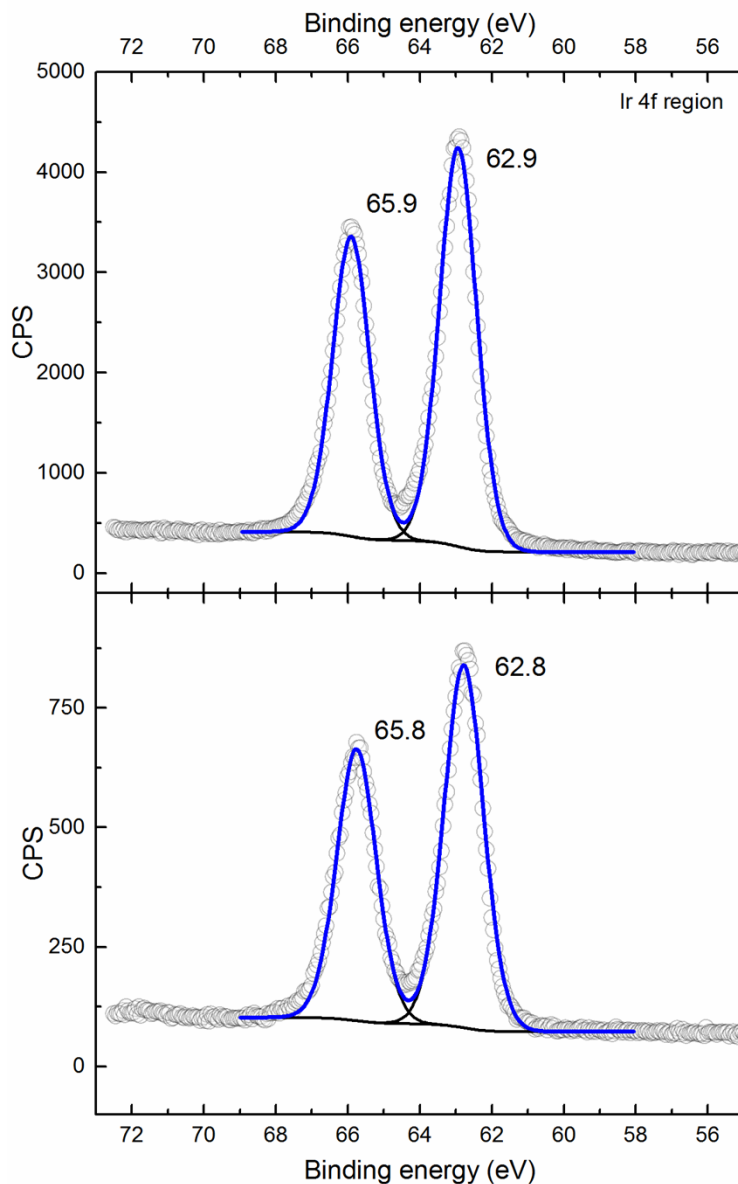


Figure S6. High-resolution XP spectra in the Ir 4f and N 1s regions for [Cp*Ir(bpy)Cl]Cl drop-cast onto Cu foil (upper panels) and for the mixed methyl/bipyridyl surface exposed to a 20-mM solution of [Cp*IrCl₂]₂ in CH₂Cl₂ for 1 h (lower panels). Data are plotted as gray circles, and the individual fits and Shirley background are the black lines. The complete fit made up of the individual components is the blue line. The Ir 4f_{5/2} FWHM was constrained to equal that of the Ir 4f_{7/2} peak. For N 1s spectra, FWHM values for each contribution were constrained to be equal.



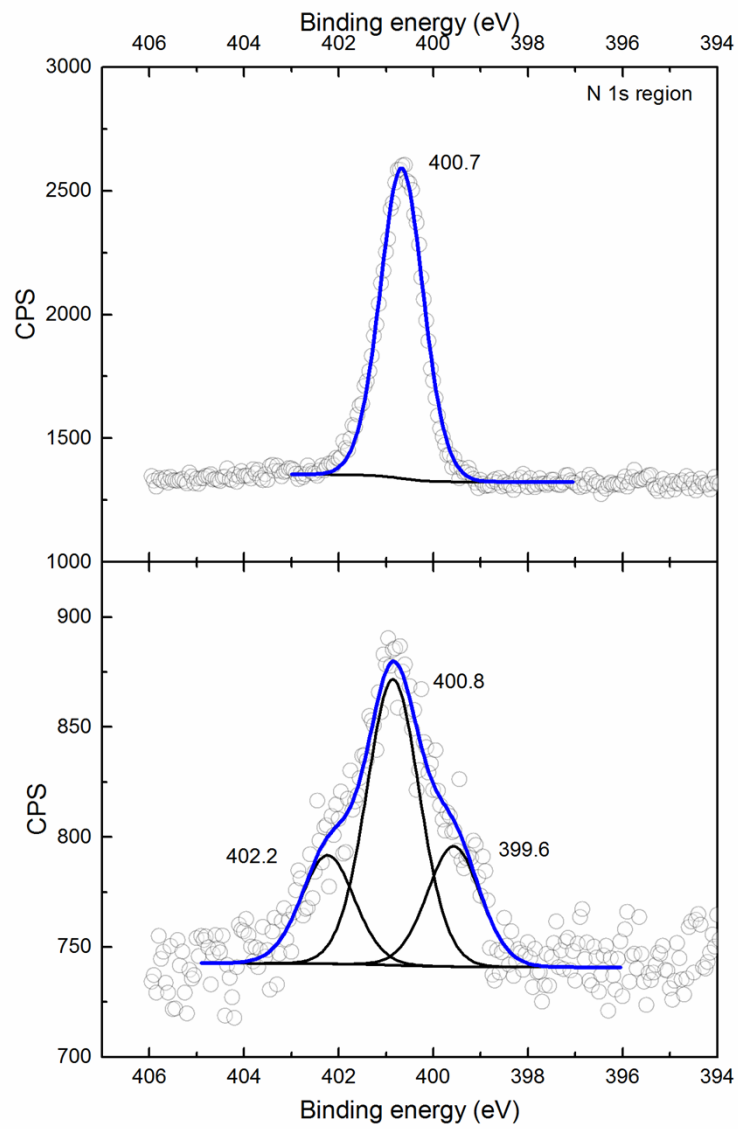


Figure S7. XP spectrum of 2,2'-bipyridyl-*N*-oxide in the N 1s region, showing contribution of the oxidized N at 403.6 eV. Data are plotted as gray circles, and the individual fits are the black lines. The complete fit made up of the individual components is the red line. The FWHM values for each contribution were constrained to be equal.

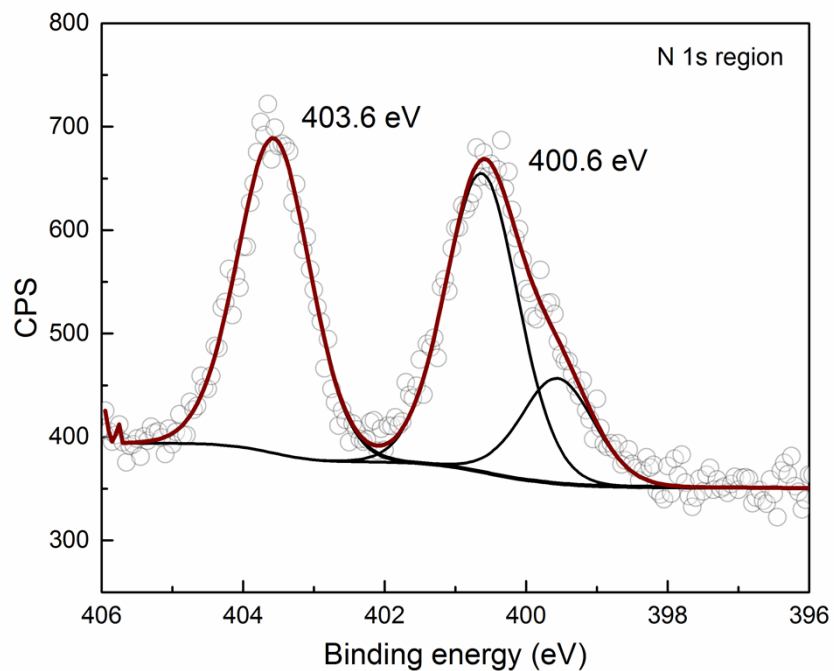


Figure S8. Comparison of Ru 3p XP spectra for a mixed methyl/bipyridyl-functionalized surface exposed overnight to $\text{Ru}(\text{acac})_2(\text{coe})_2$ (upper panel) and $[\text{Ru}(\text{acac})_2(\text{bpy})]\text{PF}_6$ drop-cast onto Cu foil (lower panel).

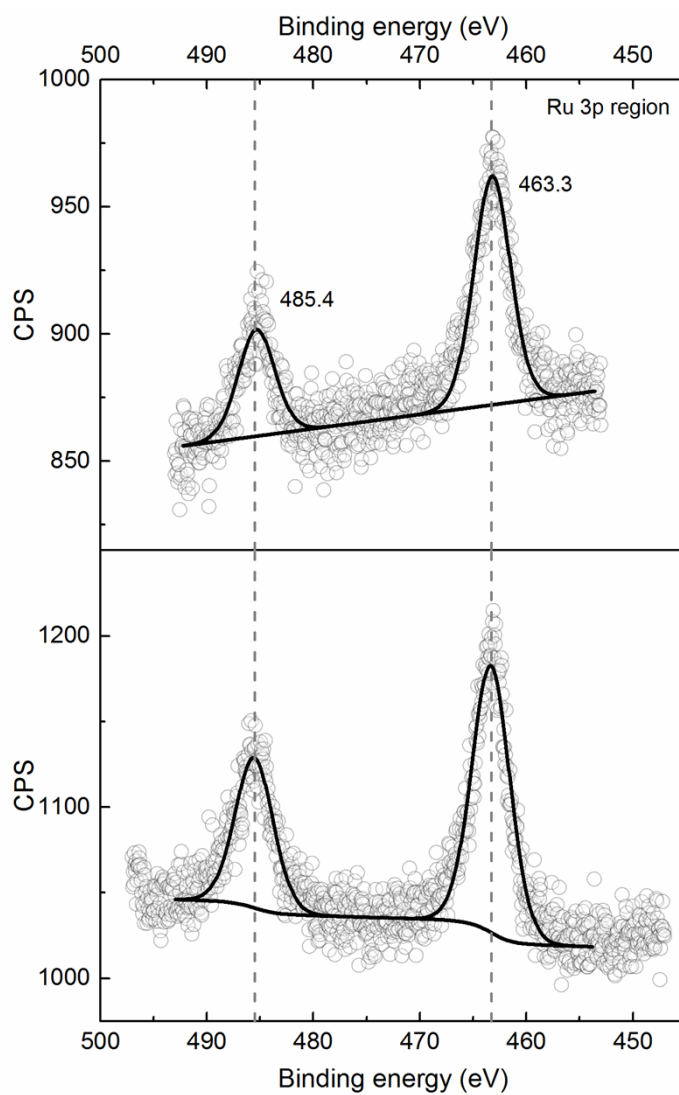


Figure S9. N 1s region XP spectra for a metallated surface (upper panel) and for the Ru model compound **6** (lower panel). Data are plotted as gray circles, and the individual fits are the black lines. The complete fit made up of the individual components is a black line. The FWHM values for each contribution were constrained to be equal.

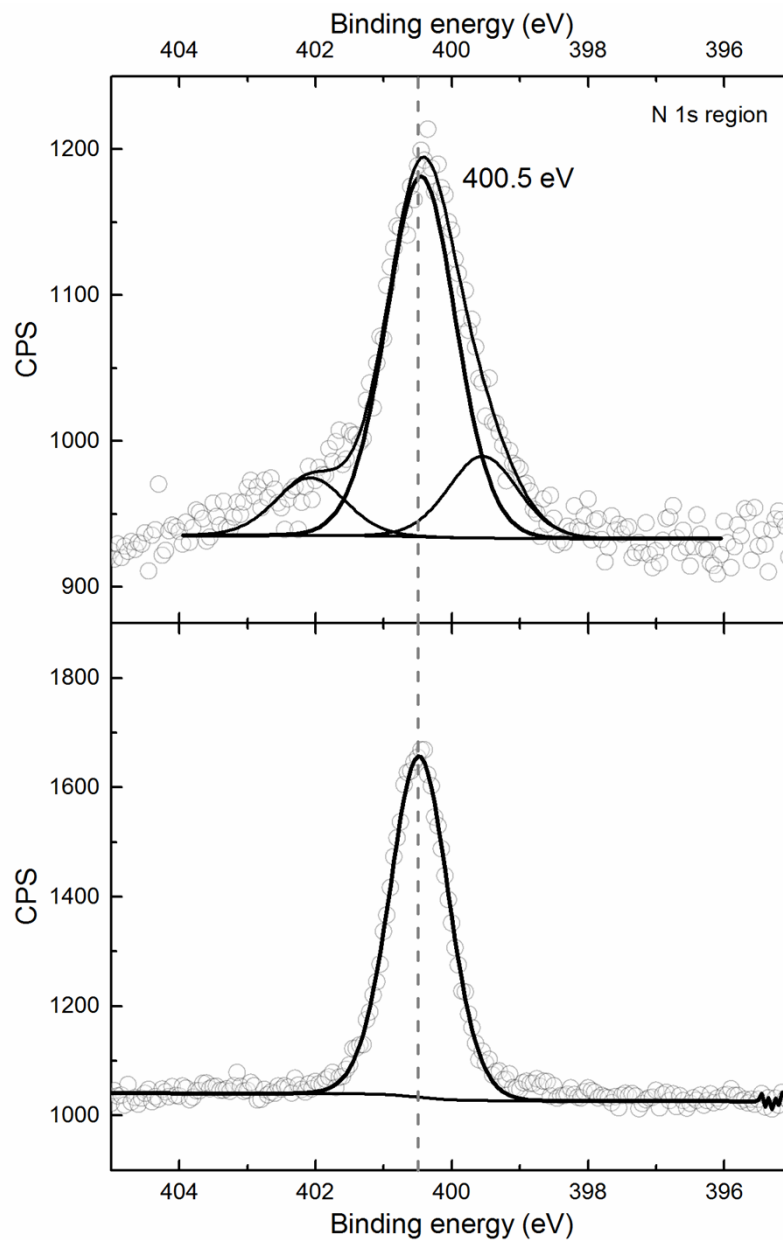


Figure S10. Cyclic voltammetry data collected with the mixed methyl/ferrocenyl surface from +0.4 to -2.0 V vs. $\text{Fc}^{+/0}$ at 100 mV/s.

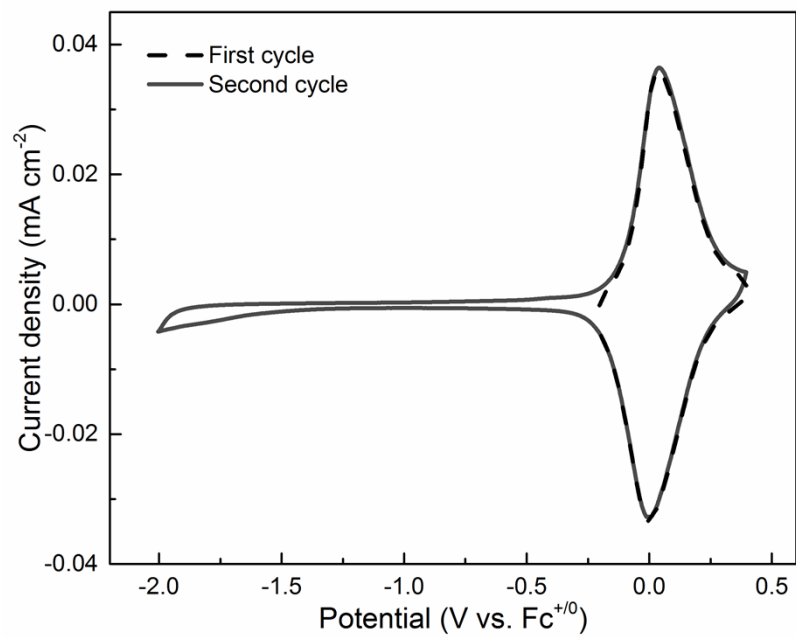


Figure S11. Comparison of cycles 2 (gray line) and 3 (green line) of voltammetry carried out on the mixed vinylferrocenyl/methyl surface. The voltammograms are virtually identical, demonstrating the stability of the surface preparation.

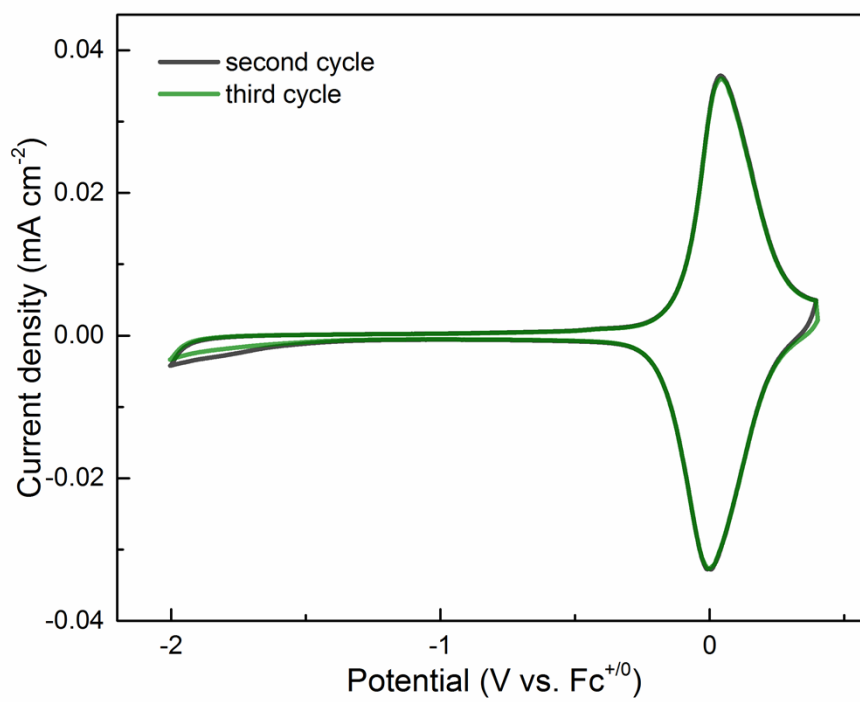


Figure S12. Electrochemical response of **3** in acetonitrile solution with (n-Bu)₄NPF₆ as supporting electrolyte. Left panel: selected cyclic voltammograms at scan rates between 50 and 200 mV s⁻¹. Right panel: linear dependence of peak current (filled circles: cathodic; open circles: anodic) on the square root of the scan rate.

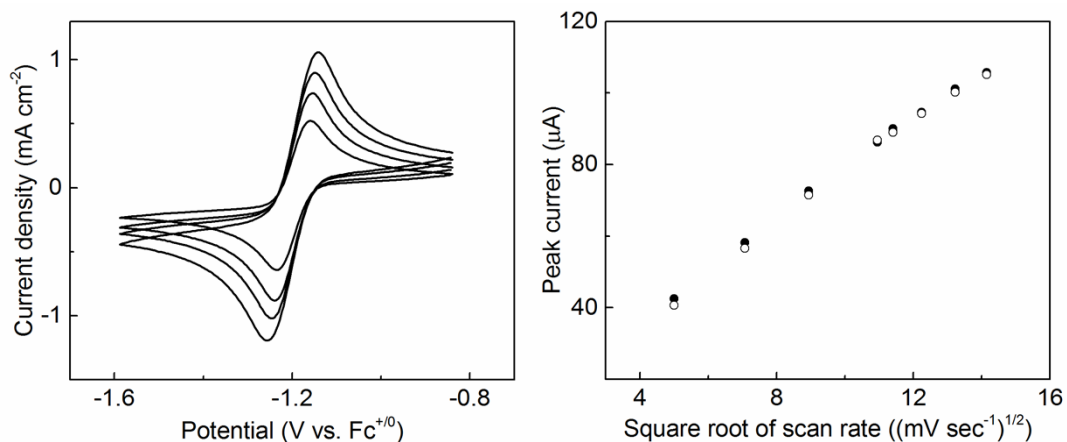


Figure S13. Electrochemistry of Rh complex **3** in solution and upon addition of *p*-toluenesulfonic acid.

Conditions: [Rh] = 10⁻³ M; 0.1 M (n-Bu)₄NPF₆ in CH₃CN; basal-plane graphite working electrode; Pt counter; Ag/Ag⁺ pseudoreference electrode with ferrocene as external standard.

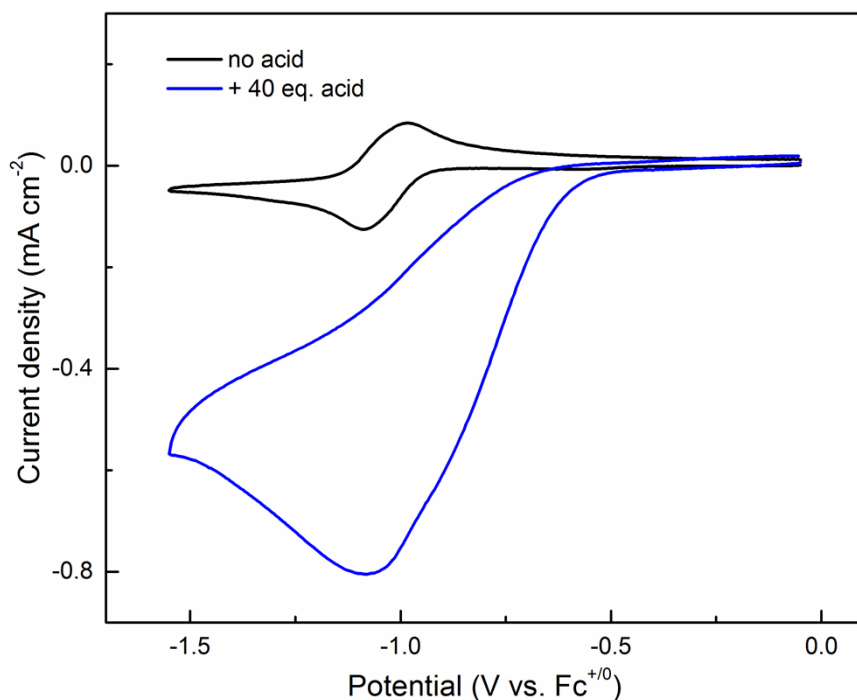


Figure S14. Electrochemical response of a methyl/bipyridyl surface modified with $[\text{Cp}^*\text{RhCl}_2]_2$. Black dashed line: first cycle of voltammetry; gray solid line: second cycle; black solid line: sixth cycle. See Experimental Details (above) for detailed conditions.

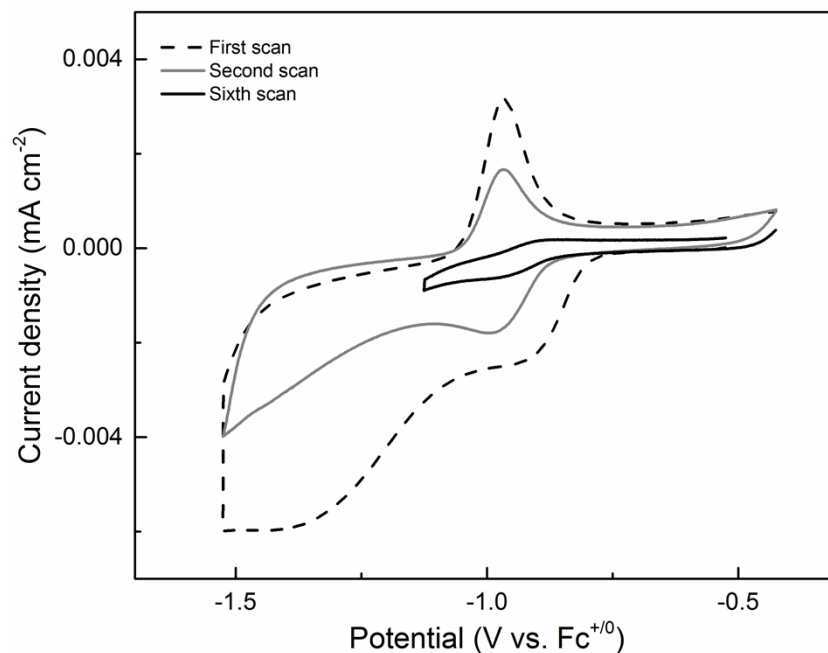


Figure S15. Electrochemical response of a methyl/bipyridyl surface modified with $[\text{Cp}^*\text{RhCl}_2]_2$. Cycles as described in figure legend.

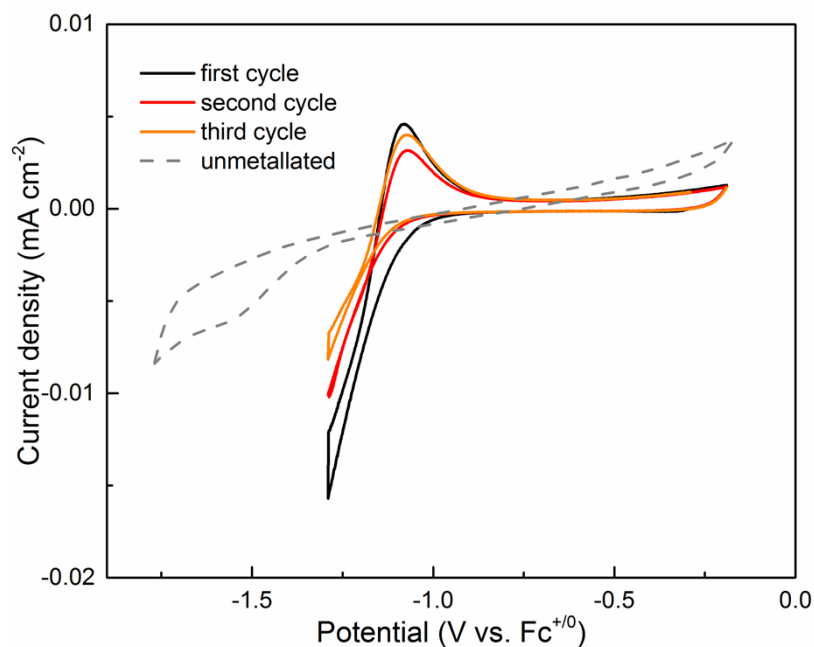


Figure S16. XPS of methyl/bipyridyl surface metallated with $[\text{Cp}^*\text{RhCl}_2]_2$ showing the loss of both Rh and N following electrochemistry. Data for the Rh 3d region are plotted as a black line, with no apparent peaks. N 1s data are plotted as gray circles, and the fit to a single N 1s peak is plotted as a blue line.

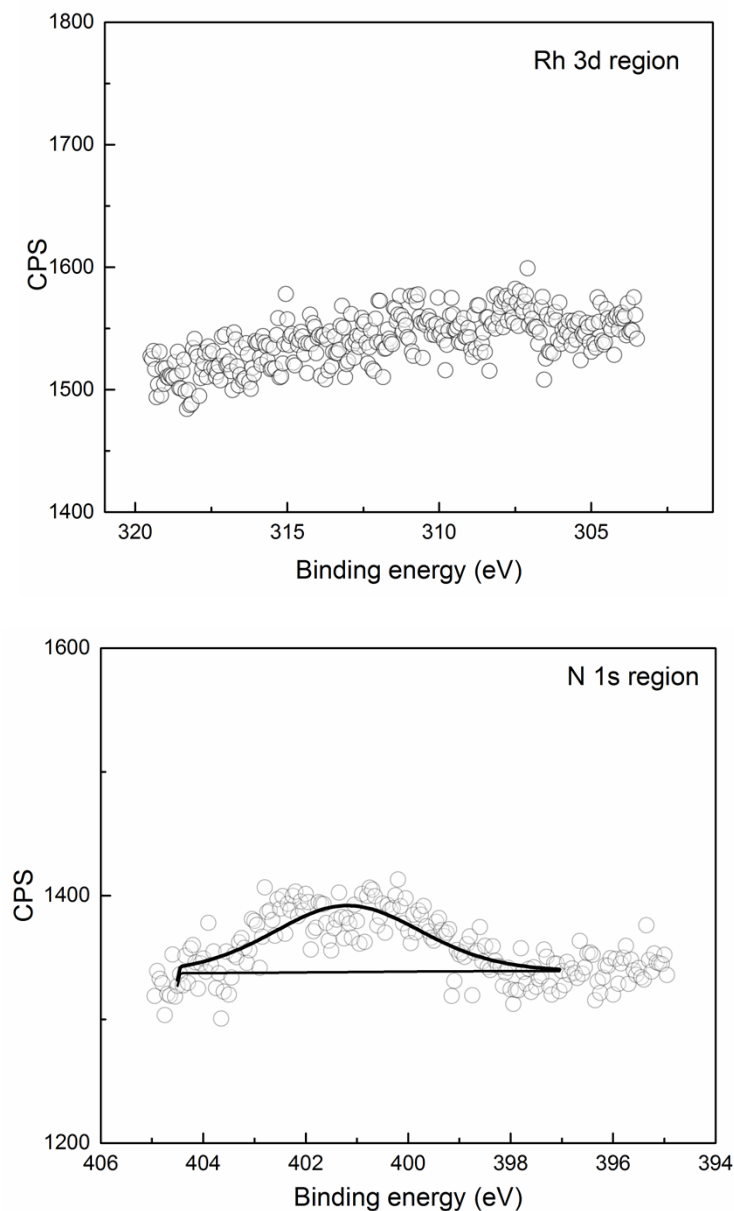


Figure S17. Ru model **5** electrochemistry in solution. Conditions: $[\text{Ru}] = 10^{-3} \text{ M}$; $0.1 \text{ M (n-Bu)}_4\text{NPF}_6$ in CH_3CN ; basal-plane graphite working electrode; Pt counter; Ag/Ag^+ pseudoreference electrode with ferrocene as external standard. Top panel: cyclic voltammetry. Lower panel: Peak currents from scan rate-dependent voltammetry. The data confirm the diffusional nature of the soluble model compound **5**.

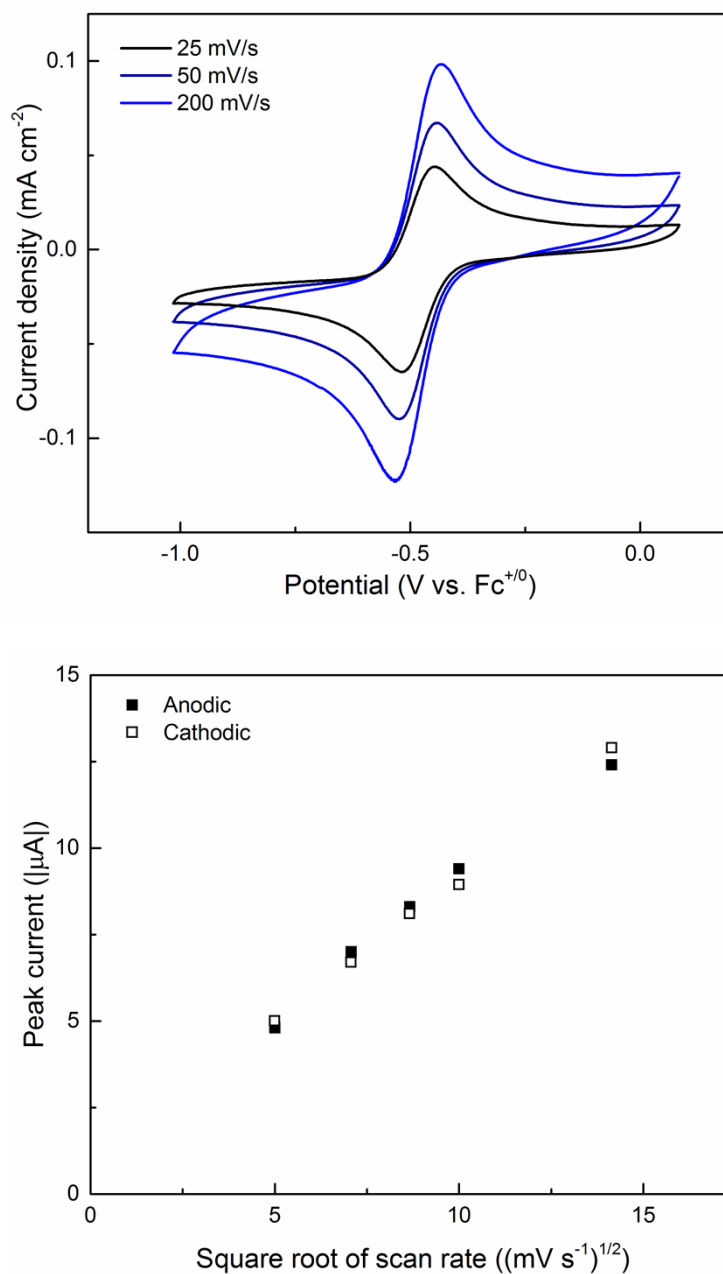
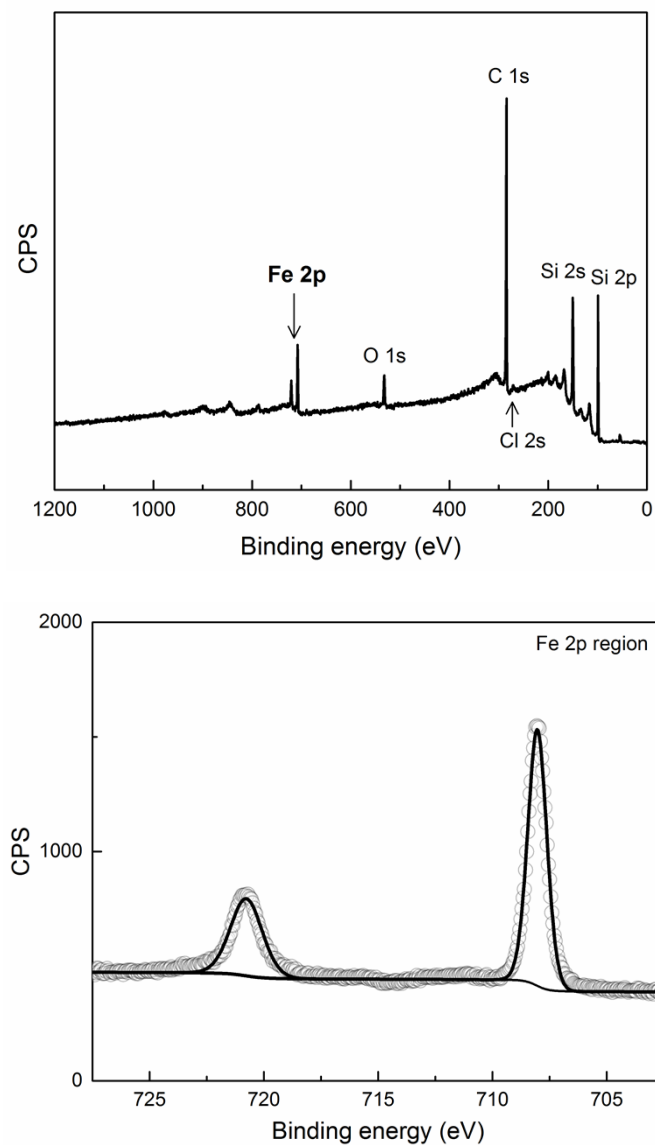
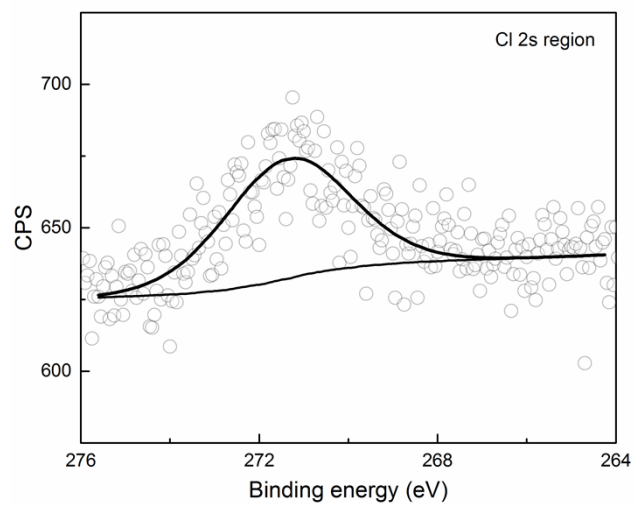
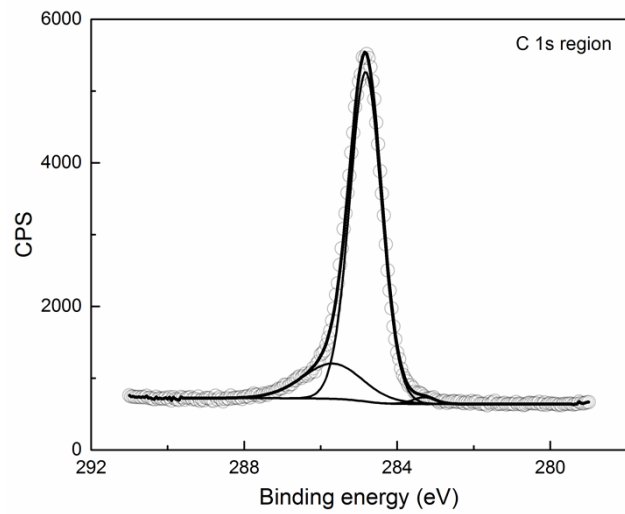
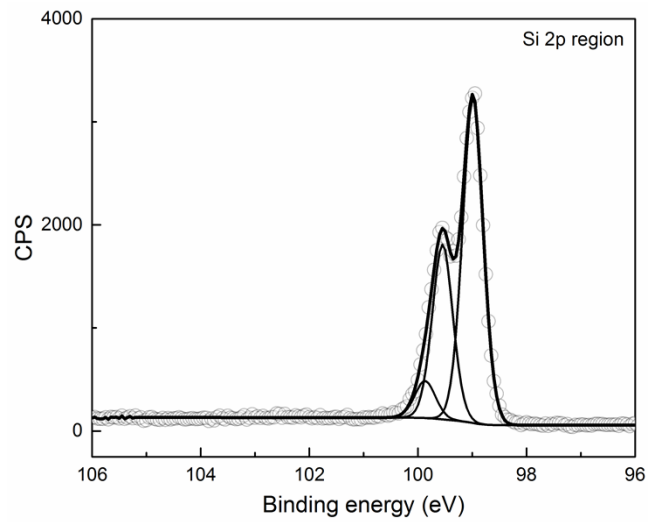


Figure S18. XPS characterization of the mixed vinylferrocenyl/methyl surface as described in the main text. For the survey spectrum, data are plotted as the black line. For the Fe 2p, Si 2p, C 1s, and Cl 2s spectra, data are plotted as gray circles, and peak contributions are plotted as black lines.





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